



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :

C09K 5/00

A1

(11) International Publication Number:

WO 99/37733

(43) International Publication Date:

29 July 1999 (29.07.99)

(21) International Application Number:

PCT/SE99/00086

(22) International Filing Date:

22 January 1999 (22.01.99)

(30) Priority Data:

9800152-2

22 January 1998 (22.01.98)

SE

(71) Applicant (for all designated States except US): ASPEN
PETROLEUM AB [SE/SE]; Sjöportsgatan 2, S-417 64
Göteborg (SE).

(72) Inventor; and

(75) Inventor/Applicant (for US only): STARZMANN, Martin
[SE/SE]; Skårgatan 68, S-412 69 Göteborg (SE).(74) Agents: ASSADI, Behdad et al.; Göteborgs Patentbyrå Dahls
AB, Sjöporten 4, S-417 64 Göteborg (SE).(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,
GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ,
LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW,
MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL,
TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO
patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR,
IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF,
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

In English translation (filed in Swedish).

(54) Title: FROST RESISTANT HEATING/COOLING FLUID

(57) Abstract

Frost resistant, aqueous cooling/heating fluid containing alkali salts of acetic acid and/or formic acid and which as a corrosion inhibitor contains a mixture of a C₅-C₁₆ monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, a C₅-C₁₆ dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

5

Frost resistant heating/cooling fluid

Technical field

10 The present invention relates to a frost resistant, aqueous heating/cooling fluid, containing alkali salts of acetic acid and/or formic acid. The heating/cooling fluid is intended for transport of cold or heat in industrial cooling plants, cooling systems in vessels and vehicles, cooling systems for skating ice in sports centres, heat exchangers, district heating systems, heat pumps, solar panels etc.

15

Background of the invention

In aqueous heating/cooling fluids, frost resistance is usually obtained by means of an addition of ethylene glycol. Ethylene glycol is a liquid which is mixable with water to any extent, exhibits a low risk of fire and explosion, and is frost resistant and also colourless and odourless. The lowest solidifying point (-57 °C) of a glycol-water mixture is at a
20 ethylene glycol content of 60 volume-%. However, the disadvantage with ethylene glycol is its high degree of toxicity. Thereby, it poses an environmental threat if it ends up in the sea, lakes and streams, for instance, if cooling liquid is discharged or leaks out.

25 From EP-B-0 306 972, a partially or completely glycol-free, aqueous cooling fluid is known, which contains an addition of sodium acetate and sodium formate or potassium acetate and potassium formate in certain ratios. By means of this fluid composition, a freezing temperature pf -70 °C or lower can be obtained. The fluid composition exhibits all the advantages with the conventional glycol-water mixture, at the same time as it does
30 not exhibit its toxicity.

However, the above-mentioned cooling fluid contains strong ions, wherein it is very important to have a good corrosion protection. In EP-B-0 306 972, it is disclosed that benzoic acid, sodium benzoate, potassium benzoate or benzotriazole are used for corrosion

protection. These are film-forming chemicals. The formed film protects metal surfaces from corrosion attacks. In order not to risk local corrosion attacks, the film layer has to be intact across the entire metal surface. A disadvantage with the film is an impaired heat transfer between the metal surface and the cooling fluid.

5

Purpose of the invention and most important features

The purpose of the present invention is to provide a corrosion protected heating/cooling fluid of the above-mentioned type, which exhibits an effective heat transfer between metal surface and fluid, at the same time as the corrosion protection is excellent. This has been achieved by means of the fluid containing a corrosion inhibitor in the form of a mixture of a C₅-C₁₆ monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, a C₅-C₁₆ dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole.

The content of alkali salts of acetic acid and/or formic acid in the heating/cooling fluid should preferably be between 5 and 50 weight-%, calculated on the total weight of the fluid.

The heating/cooling fluid contains between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-% of the above-mentioned corrosion inhibitor, calculated on the total weight of the alkali salts of acetic acid and/or formic acid.

Summary of the invention

From the above-mentioned EP-B-0 306 972, it is known that an addition of alkali salts of certain anions, mainly acetates and formates, to water results in a strong depression of freezing-point of an aqueous medium. The depression of freezing-point becomes particularly large at certain mixing ratios of the included salts.

The heating/cooling fluid according to the invention contains between 5 and 50 weight-% alkali salts of acetic acid and/or formic acid calculated on the weight of the fluid, primarily sodium acetate, potassium acetate, sodium formate and/or potassium formate. The included salts can be present in any mutual mixing ratio, i.e. only one of the salts or two or several salts in a mixture together. Partly depending on the total salt content, and partly on the

mixing ratio of the salts, different depressions of freezing-point of the fluid is obtained. Also other freezing-point depressing additions can be included in the fluid, e.g. urea.

5 The heating/cooling fluid according to the invention is a strong ionic solution, wherein the significance of an efficient corrosion protection is particularly large. EP-B-0 306 972 discloses an addition of a corrosion inhibitor in the form of benzoic acid, sodium benzoate, potassium benzoate or benzotriazole, which are film-forming chemicals which create a protective film on metals surfaces and thereby protects them from corrosion attacks. As mentioned above, the disadvantages with this type of corrosion inhibitors is partly that the
10 film layer must be intact across the entire metal surface in order to make the corrosion protection effective and to avoid local corrosion attacks, and partly that the heat transfer between metal surface and heating/cooling fluid is impaired.

15 According to the invention, it has now surprisingly been found that, in addition to an excellent corrosion protection, an addition of a corrosion inhibitor in the form of a mixture of a C₅-C₁₆ monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole, furthermore provides an excellent heat transfer between the metal surface and the fluid.

20 A corrosion inhibitor of this type is disclosed in US-A-4,647,392. According to this document, the corrosion inhibitor is intended to be used in glycol-water mixtures. The use as a corrosion inhibitor in salt solutions of the type which the invention relates to, however, is not disclosed in the U.S. patent.

25 The amounts of the components included in the corrosion inhibitor can vary between 0.02 and 3 weight-%, calculated on the weight of the fluid, for both the monocarboxylic acid and the dicarboxylic acid or the alkali-, ammonium-, or amino-salts of said acid. The amount of triazole can vary between 0.02 and 2 weight-%, calculated on the total weight of the fluid.

30 The total content of the corrosion inhibitor should be between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-%, calculated on the weight of the fluid.

The corrosion inhibitor comprises a mixture of three basic components, namely a monocarboxylic acid, a dicarboxylic acid and a triazole. The monocarboxylic acid is preferably an aliphatic C₅-C₁₆ monocarboxylic acid, preferably selected from the group of octanoic acid, nonanoic acid, decanoic acid, undecanoic acid or dodecanoic acid, 2-ethyl
5 hexanoic acid and neodecanoic acid.

The dicarboxylic acid is preferably either a C₈-C₁₂ aliphatic dicarboxylic acid selected from the group of suberic acid, azelaic acid, sebacic acid, undecanoic di-acid, dodecanoic di-acid and the di-acid of di-cyclopentadienylidene or a C₈-C₁₂ aromatic dicarboxylic acid,
10 preferably terephthalic acid.

The triazole is preferably tolyltriazole or benzotriazole.

In comparison with using only one of the acid types, the combination of mono- and
15 dicarboxylic acid or its salts provides a synergistic effect when the corrosion protection of metallic surfaces is concerned. The triazole is specifically used as a copper protection.

Other conventional corrosion-inhibiting components can of course also be included in the heating/cooling fluid according to the invention.

20

Example

In order to test the heat transfer characteristics, a system in which the liquid which is to be tested is circulating with a constant volume flow under constant pressure was used. This liquid passes a metal coupon onto which a heating device is applied. The temperature of
25 the liquid is kept constant by means of a cooling coil. The temperature of the metal coupon is measured and recorded over time. An increase of the temperature in the metal coupon indicates a relative impairment of the heat transfer ability over the same time.

The liquids which were tested exhibited the following compositions:

30

	INCLUDED COMPONENTS (weight-%)	Reference - Cooling fluid with conventional inhibitor	Test - Cooling fluid with inhibitor according to the invention
5	Water	49.8	60
	Potassium acetate	31.2	31.2
	Potassium formate	7.8	7,8
	Sodium benzoate	1.1	-
	Tolyoltriazole	1.7	-
10	Borax	0.3	-
	Sodium meta-phosphate	1	-
	Sodium nitrate	1.8	-
	Sodium silicate	0.3	-
	Glycerol	5	-
15	Corrosion inhibitor acc. to the invention	-	1

The following results were obtained for the heat transfer characteristics:

	Test duration (h)	Reference Coupon temperature (°C)	Reference Coupon temperature (°C)
20	0	170	170
	10	181	171
	20	183	171
	30	184	171.5
25	40	186	171
	45	188	171.5

As is evident from these results, the test liquid, which comprised an addition of a corrosion inhibitor according to the invention, gave a very small increase of the temperature in the

metal coupon over time, something which indicates a maintained effective heat transfer between the metal surface and the fluid. The reference, however, which contained a conventional corrosion inhibitor essentially in accordance with EP 306,972, exhibited a significant increase of the temperature in the metal coupon in the course of time and, accordingly, a relative impairment of the heat transfer ability in the same time period.

This difference is thought to be the result of the corrosion inhibitor in the reference fluid forming a film between fluid and metal surface, which impairs the heat transfer. It is presumed that such a film formation, however, does not take place when utilizing the corrosion inhibitor according to the invention.

5 **Claims**

1. A frost resistant heating/cooling fluid containing alkali salts of acetic acid and/or formic acid,
c h a r a c t e r i z e d i n that it also contains a corrosion inhibitor in the form of a mixture
10 of a C₅-C₁₆ monocarboxylic acid or alkali-, ammonium-, or amino-salts of said acid, a C₅-C₁₆ dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, and also a triazole.
2. A cooling fluid according to claim 1,
c h a r a c t e r i z e d i n that it contains between 5 and 50 weight-% alkali salts of acetic
15 acid and/or formic acid calculated on the weight of the fluid.
3. A cooling fluid according to claim 1 or 2,
c h a r a c t e r i z e d i n that it contains between 0.4 and 10 weight-%, preferably between 0.5 and 2 weight-% of the corrosion inhibitor, calculated on the total weight of the cooling
20 fluid.
4. A cooling fluid according to any one or any of the preceding claims,
c h a r a c t e r i z e d i n that it contains between 0.02 and 3 weight-% of the monocarboxylic acid or alkali-, ammonium- or amino-salts of said acid, calculated on the
25 total weight of the cooling fluid.
5. A cooling fluid according to claim 4,
c h a r a c t e r i z e d i n that it contains between 0.02 and 3 weight-% of the dicarboxylic acid or alkali-, ammonium- or amino-salts of said acid, calculated on the total weight of
30 the cooling fluid.
6. A cooling fluid according to claim 4 and 5,
c h a r a c t e r i z e d i n that it contains between 0.02 and 2 weight-% triazole calculated on the total weight of the cooling fluid.

7. A cooling fluid according to any one of any of the preceding claims,
c h a r a c t e r i z e d i n that said monocarboxylic acid is an aliphatic C_5 - C_{16}
monocarboxylic acid, preferably selected from the group of octanoic acid, nonaic acid,
decanoic acid, undecanoic acid or dodecanoic acid; 2-ethyl hexanoic acid and neodecanoic
5 acid.

8. A cooling fluid according to any one or any of the preceding claims,
c h a r a c t e r i z e d i n that said dicarboxylic acid is a C_8 - C_{12} aliphatic dicarboxylic acid
selected from the group of suberic acid, azealic acid, sebacic acid, undecanoic di-acid,
10 dodecanoic di-acid and the di-acid of di-cyclopentadienylide.

9. A cooling fluid according to any one or any of the preceding claims,
c h a r a c t e r i z e d i n that said dicarboxylic acid is a C_8 - C_{12} aromatic dicarboxylic
acid, preferably terephthalic acid.

10. A cooling fluid according to any one or any of the preceding claims,
c h a r a c t e r i z e d i n that the triazole is tolyoltriazole or benzotriazole.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 99/00086

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C09K 5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

QUESTEL: EDOC, WPIL, JAPIO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0306972 A1 (ESZAKMAGYARORSZÁGI VEGIMŰVEK), 15 March 1989 (15.03.89), claims 1-3 --	1-10
A	US 4647392 A (JEROME W.DARDEN ET AL), 3 March 1987 (03.03.87), column 3, line 53 - column 4, line 53 -- -----	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

& document member of the same patent family

Date of the actual completion of the international search

21 April 1999

Date of mailing of the international search report

06 -05- 1999

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM

Authorized officer

Benat Christensson

INTERNATIONAL SEARCH REPORT
Information on patent family members

02/03/99

International application No.
PCT/SE 99/00086

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0306972 A1	15/03/89	SE 0306972 T3 DE 3871668 A FI 884135 A JP 1103684 A	09/07/92 11/03/89 20/04/89
US 4647392 A	03/03/87	CA 1258162 A EP 0229440 A,B SE 0229440 T3 JP 62158778 A	08/08/89 22/07/87 14/07/87